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JP11-089708

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CLAIMS

[Claim(s)]

[Claim 1] (1) Water, (2) abrasives, (3) nitric acids, a nitrous acid, a hydrochloric acid, perchloric acid, a chloric acid, A chlorous acid, a hypochlorous acid, a boric acid, perboric acid, a sulfuric acid, a sulfurous acid, persulfuric acid, The ion of a phosphoric acid, phosphorous acid, hypophosphorous acid, a silicic acid, organic acids, and those hydro acid, or those mixture -- since -- at least one kind of cation chosen from the group which consists of at least one kind of anion chosen from the becoming group, (4) ammonium ion, alkali-metal ion, and alkaline-earth-metal ion. The constituent for polish characterized by being the constituent for polish which becomes by *****, and the total amount of the cation of (4) being 0.001-0.15 mols/l.

[Claim 2] The constituent for polish according to claim 1 whose content of abrasives is less than 40 % of the weight on the basis of the weight of the constituent for polish.

[Claim 3] The constituent for polish given in either of claims 1 or 2 which is at least one kind of abrasives chosen from the group which abrasives become from a silicon dioxide, an aluminum oxide, cerium oxide, titanium oxide, silicon nitride, a zirconium dioxide, and a manganese dioxide.

[Claim 4] The constituent for polish given in any 1 term of claims 1-3 which is at least one kind of cation chosen from the group which a cation becomes from NH_4^+ , Li^+ , Na^+ , K^+ , Be^{2+} , Mg^{2+} , and calcium^{2+} .

[Claim 5] The constituent for polish given in any 1 term of claims 1-4 whose total amount of a cation is 0.005-0.1 mols/l.

[Claim 6] The constituent for polish given in any 1 term of claims 1-4 whose total amount of a cation is 0.01-0.075 mols/l.

[Claim 7] The constituent for polish given in any 1 term of claims 1-6 whose total amounts of said anion are 1/2 in a mole ratio to said cation. [200-2]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the suitable constituent for polish for surface flattening processing of the device wafer especially in semiconductor industry etc. about the constituent for polish used for polish of various industrial products, such as a semi-conductor, a photo mask, various bases for memory hard disks, and synthetic resin, or the member of those.

[0002] In more detail, in polish of the silicon-dioxide film which is an insulator layer for the interlayer insulation film and isolation to which the CMP technique (detail postscript) is applied conventionally, this invention can make the polish front face excellent in the homogeneity in a wafer form, and relates to the constituent for polish applicable to an advanced device formation technique at the same time a big polish rate is obtained.

[0003]

[Description of the Prior Art] The so-called advance of high-tech products including a computer in recent years is remarkable, and the components used for this, for example, ULSI, and ***** high integration and improvement in the speed are being enhanced. In connection with this, as for the design rule of a semiconductor device, detailed-ization progresses every year, the depth of focus in a device manufacture process becomes shallow, and the surface smoothness required of a pattern formation side is becoming severe.

[0004] Moreover, although compaction of the wire length by multilayering of a device is performed in order to cope with buildup of the wiring resistance by detailed-izing of wiring, the level difference on the formed front face of a pattern has been becoming an issue as a failure of multilayering.

[0005] In performing such detailed-izing and multilayering, it is required in that process to perform flattening on the front face of a request for removing a level difference, and a spin-on glass, resist etchback, and other flattening methods were used as this technique until now.

[0006] However, by such technique, although partial flattening is possible, it is in a difficult situation to attain global pre nari ZESHON (perfect flattening) required of a next-generation device, and flattening (it is called "CMP" Chemical Mechanical Polishing and the following) by mechanical mechanochemical-polishing processing which was, carried out and combined physical polish and chemical polish is examined increasingly current.

[0007] The technical technical problem which hits carrying out flattening of the silicon-dioxide film which is an insulator layer for an interlayer insulation film or isolation using such a polish technique is raising productivity by grinding the field which carries out flattening processing at making homogeneity the neither more nor less and the big polish rate of the machining allowance by polish.

[0008] Conventionally, the constituent for polish containing the basic compound chosen from fumed silica, water and a potassium hydroxide, ammonia, and others has been used for polish of the silicon-dioxide film currently used for the insulator layer for an interlayer insulation film or isolation. When using such a constituent for polish, a polish rate can be enlarged if the quantity of the addition of a basic compound is increased.

[0009] This is because chemical scouring is used in such polish processing. Chemical scouring will mean that the silicon-dioxide film becomes easy to receive clearance by polish according to the effectiveness of the basic compound which is a chemical polish accelerator in response to chemical pervasion, if the above-mentioned polish processing is taken for an example. That is, in the above-mentioned polish processing, by increasing the quantity of the addition of a basic compound, a chemical operation increases and the whole polish rate becomes large.

[0010]

[Problem(s) to be Solved by the Invention] However, although usually comparatively a lot of basic compounds are included and the polish rate of need level was maintained in the conventional constituent for polish which was described above as far as this invention persons get to know, in the homogeneity of a polished surface, it could not be made sufficiently satisfactory level, but there was still room of amelioration. Therefore, a constituent for polish compatible in sufficient polish rate and the homogeneity of a polished surface was desired.

[0011]

[Means for Solving the Problem]

[Summary of the Invention]

The constituent for polish of <summary> this invention (1) water, (2) abrasives, (3) nitric acids, A nitrous acid, a hydrochloric acid, perchloric acid, a chloric acid, a chlorous acid, a hypochlorous acid, a boric acid, Perboric acid, a sulfuric acid, a sulfurous acid, persulfuric acid, a phosphoric acid, phosphorous acid, hypophosphorous acid, The ion of a silicic acid, organic acids, and those hydro acid, or those mixture, since -- at least one kind of anion chosen from the becoming group, and (4) ammonium ion -- It is the constituent for polish which comes to contain at least one kind of cation chosen from the group which consists of alkali-metal ion and alkaline-earth-metal ion, and is characterized by the total amount of the cation of (4) being 0.001-0.15 mols/l.

[0012] The polished surface in which the constituent for polish of <effectiveness> this invention had the large polish rate, and homogeneity was simultaneously excellent can be made to form.

[0013] [Concrete explanation of invention]

Suitable abrasives to use as abrasives in the constituent for polish of <abrasives> this invention are chosen from a silicon dioxide, an aluminum oxide, cerium oxide, titanium oxide, silicon nitride, a zirconium dioxide, and the group that consists of a manganese dioxide.

[0014] In this invention, it has and that from which the manufacturing method of colloidal silica, fumed silica, and others and description differ recognizes variety existence at the silicon dioxide which can be.

[0015] There are alpha-alumina, delta alumina, theta alumina, kappa alumina, and a different thing like other gestalten also in an aluminum oxide. Moreover, there are some which are called a fumed alumina from a manufacturing method.

[0016] It sees in cerium oxide from a thing trivalent from the oxidation number, a tetravalent thing, and crystal system, and there is a thing of hexagonal system, a tesseral system, and a face-centered cubic system in it.

[0017] It sees in titanium oxide from crystal system, and there is a thing of titanium monoxide, 3 oxidization 2 titanium, a titanium dioxide, and others in it. Moreover, there are some which are called a fumed titania from a manufacturing method.

[0018] Silicon nitride has alpha-silicon nitride, beta-silicon nitride, amorphous silicon nitride, and a different thing like other gestalten.

[0019] A zirconium dioxide is seen from crystal system and has monoclinic system, tetragonal system, and an amorphous thing. Moreover, there are some which are called fumed zirconia from a manufacturing method.

[0020] A manganese dioxide is seen in gestalt and has alpha-manganese dioxide, beta-manganese dioxide, gamma-2 manganese oxide, delta-2 manganese oxide, epsilon-2 manganese oxide, eta-2 manganese oxide, and others.

[0021] These things can be combined and used for the constituent of this invention at arbitration if needed. When combining, especially the how to combine or rate to be used are not limited.

[0022] The above-mentioned abrasives grind a polished surface-ed according to an operation [mechanical / as an abrasive grain]. among these, generally 5-500nm of 10-200nm of particle size of a silicon dioxide comes out preferably with the mean particle diameter called for from the specific surface area measured with the BET adsorption method. moreover, generally an aluminum oxide, a zirconium dioxide, titanium oxide, silicon nitride, and 10-5,000nm of 50-3,000nm of particle size of a manganese dioxide come out preferably with the mean particle diameter called for from the specific surface area measured with the BET adsorption method. furthermore, the particle size of cerium oxide is the mean particle diameter observed by the scanning electron microscope, and, generally comes out 50-3,000nm preferably 10-5,000nm.

[0023] A polish rate becomes extremely small and is not practical if smaller than the range which there is a between title of the surface roughness of the ground front face being large when the mean particle diameter of these abrasives is large across the range shown here, or a scratch occurring, and was shown in reverse here.

[0024] the content of the abrasives in the constituent for polish -- criteria [weight / of a constituent] -- carrying out -- less than 40 % of the weight -- it comes out one to 30% of the weight more preferably 0.1 to 40% of the weight. If remainder has few contents of abrasives, a polish rate will become small; when many [to remainder], it becomes impossible to maintain homogeneity distribution, constituent viscosity may become excessive, and handling may become difficult at reverse.

[0025] the constituent for polish of <anion> this invention -- the ion of a nitric acid, a nitrous acid, a hydrochloric acid, perchloric acid, a chloric acid, a chlorous acid, a hypochlorous acid, a boric acid, perboric acid, a sulfuric acid, a sulfurous acid, persulfuric acid, a phosphoric acid, phosphorous acid, hypophosphorous acid, a silicic acid, organic acids, and those hydro acid, or those mixture -- since -- it comes to contain at least one kind of anion chosen from the becoming group As for these anions, it is common to make it generate in the constituent for polish by dissolving the acid compound which dissolves in water and emits the aforementioned specific anion, i.e., an acid, and its salt. Moreover, since a main solvent is water, the above-mentioned ion may be made to generate in this invention by introducing into water directly the gas-like compound which dissolves in water and emits the aforementioned anion, for example, hydrochloric acid gas, a sulfur dioxide, and others.

[0026] The thing of arbitration can be used for the acid compound to be used if effectiveness of this invention is not spoiled. Specifically (1) nitric acid, a nitrous acid, a hydrochloric acid, perchloric acid, a chloric acid, a chlorous acid, A hypochlorous acid, a boric acid, perboric acid, a sulfuric acid, a sulfurous acid, persulfuric acid, a phosphoric acid, phosphorous acid, hypophosphorous acid, a silicic acid, or an organic acid (for example, a formic acid --), for example, a carboxylic acid An acetic acid, monochloroacetic acid, dichloroacetic acid, a trichloroacetic acid, a maleic acid, A fumaric acid, a glycolic acid, a citric acid, a malic acid, a lactic acid, a tartaric acid, a malonic acid, The ammonium salt of a succinic acid, a gluconic acid, a propionic acid, butanoic acid or a valeric acid, and the acid of (2) and (1), Hydrogen salt ** of two or more acids is mentioned for basicity among the acids of sodium salt, potassium salt, lithium salt, a beryllium salt, magnesium salt or a calcium salt (3), and (1). In these, especially hydro acid salt ** that consists of the ammonium salt of a nitric acid, a hydrochloric acid, a boric acid, a sulfuric acid, a phosphoric acid, a formic acid, an acetic acid, a trichloroacetic acid, a maleic acid, a fumaric acid, a glucol acid, a citric acid, a malic acid, a lactic acid, a tartaric acid, a malonic acid, a succinic acid, a gluconic acid, propionic acids, and these acids and potassium salt or a boric acid, a sulfuric acid, a phosphoric acid, a maleic acid, a fumaric acid, a glucol acid, a citric acid, a malic acid, a lactic acid, a tartaric acid, a malonic acid or a succinic acid, and ammonium ion or potassium ion is desirable. These acid compounds can also be used together at a rate of arbitration.

[0027] In the constituent for polish of this invention, although the concentration of the aforementioned specific anion is not limited unless the effectiveness of this invention is spoiled, it is desirable that the total amounts of the aforementioned specific anion are 1/2 in a mole ratio to the total amount of the below-mentioned cation as a relative amount with the cation mentioned later, and it is desirable that it is especially 1/1. [200-2] [100-1] Although it is in the inclination for a polish rate to become large by increasing the quantity of the content of a specific anion, since the dispersibility of abrasives may get

worse when it increases too much, caution is required.

[0028] Although it is more desirable to the constituent for polish of this invention to introduce an anion into the constituent for polish by using a water-soluble (soluble) acid compound from points, such as handling nature, it is possible to use, if dissolving into the constituent for polish is possible even if it is a poorly soluble compound. In other words, it is not necessary to take into consideration the acid compound which the ratio of the total amount of the aforementioned specific anion and the total amount of a cation is an amount based on the anion which is dissolving, and is not dissolving.

[0029] The constituent for polish of <cation> this invention comes to contain a specific cation. In the constituent for polish of this invention, when used, these cations are the aforementioned specific anion or independent, and promote scouring according to an operation [KEMIKARU / as a polish accelerator].

[0030] The cation used in this invention is at least one kind of cation chosen from the group which consists of ammonium ion, alkali-metal ion, and alkaline-earth-metal ion. The ion (henceforth "inorganic alkali ion") chosen from the group which consists of NH_4^+ , Li^+ , Na^+ , K^+ , Be^{2+} , Mg^{2+} , and calcium $^{2+}$ especially is desirable. Such ion is introduced into the constituent for polish by usually dissolving the basic compound which emits the aforementioned inorganic alkali ion into the constituent for polish. Although it will not be limited especially if the basic compound used here does not spoil the effectiveness of this invention, at least one kind of compound specifically chosen from the group which consists of a potassium hydroxide, ammonium hydroxide, a sodium hydroxide, a lithium hydroxide, hydroxylation beryllium, a magnesium hydroxide, and a calcium hydroxide is mentioned. These basic compounds can also be used together at a rate of arbitration. Moreover, about the above-mentioned basic compound, when metal ions other than the aforementioned inorganic alkali ion use the thing of very few high grades, since an impurity metal ion can be decreased in the constituent for polish, it is desirable.

[0031] the content of said cation of the constituent for polish of this invention -- the whole quantity of the constituent for polish -- receiving -- 0.001-0.15 mols/l. -- 0.01-0.075 mols [/] 0.005-0.1 mols /come out l. more preferably l. Although there is an inclination for a polish rate to become large by increasing the quantity of the content of said inorganic alkali ion, when many, it is in the inclination for the homogeneity of a polished surface to get worse. Furthermore, since the degree of amelioration to a polish rate etc. becomes small and may produce an economical demerit, caution is required.

[0032] The constituent for polish of <constituent for polish> this invention makes water mix and distribute the above-mentioned abrasives with desired content generally, and is prepared by carrying out the specified quantity dissolution of the compound which emits the aforementioned specific anion further, and the compound which emits the aforementioned inorganic alkali ion. The method of distributing or dissolving these components underwater is arbitrary, for example, it agitates with a wing formula agitator, or it is distributed by ultrasonic distribution. Moreover, the mixed sequence foreword of each of these components is arbitrary, and may perform first whichever of the dissolution of distribution of abrasives, and an acid compound or a basic compound, and may perform both simultaneously.

[0033] Moreover, on the occasion of preparation of the constituent for polish of this invention, various kinds of well-known additives may be added further the object which attains quality maintenance and stabilization of a product, the class of workpiece, processing conditions, and if needed on other polish processings.

[0034] That is, the following are mentioned as a suitable example of the additive added further.

(b) Celluloses, for example, a cellulose, a carboxymethyl cellulose, Hydroxyethyl cellulose and others,
 (b) water solubility alcohols, For example, ethanol, propanol, ethylene glycol, and others, A surface active agent, for example, alkylbenzene-sulfonic-acid soda, the formalin condensate of naphthalenesulfonic acid, (Ha) and -- in addition to this -- (**) -- the organic poly anion system matter, for example, a ligninsulfonic acid salt, and polyacrylate -- and -- in addition to this -- (**) -- water soluble polymers (emulsifier), for example, polyvinyl alcohol, -- and -- in addition to this -- a (**) germicide, for example, sodium alginate, -- and -- in addition to this .

[0035] Moreover, although a thing is included said bottom as abrasives, an acid compound, and a basic

compound in addition to the abrasives contained to the constituent for polish of this invention there, an acid compound, and a basic compound, it is also possible to be the objects other than the application of abrasives or a polish accelerator, for example, to use the thing of inside to others as further additive for sedimentation prevention of abrasives.

[0036] it usually comes out of the constituent for polish of this invention that pH is set to 4-10 by said addition of a principal component carried out. Although pH of the constituent for polish is changed by addition of various kinds of auxiliary additives, in order to make the effectiveness of this invention discover, it is desirable that pH is 4-10. Therefore, when pH of the constituent for polish shifts from the range of 4-10, it is desirable to add an acid or alkali and to adjust pH. Moreover, even if pH is within the limits of this, it is [other being reasons, for example, the preservation stability of the constituent for polish, being / of a polish object / the physical properties, and] sometimes desirable for it to be alike and to adjust pH more nearly further in addition to this.

[0037] In addition, although the constituent for polish of this invention can be applied to the base material of arbitration, such as various industrial products, such as a semi-conductor, a photo mask, various bases for memory hard disks, and synthetic resin, or a member of those, it is desirable to use for surface flattening processing of the device wafer especially in semiconductor industry etc.

[0038] Moreover, the constituent for polish of this invention can be prepared as a comparatively high-concentration undiluted solution, can carry out storage or transport, and it can also be diluted and used for it at the time of actual polish processing. When the above-mentioned desirable density range was indicated as a thing at the time of actual polish processing and it takes such operation, it cannot be overemphasized that it becomes a more high-concentration solution in the condition of carrying out storage or transport. Moreover, it is desirable to be manufactured with such a condensed gestalt from a viewpoint of handling nature. In addition, the concentration mentioned above indicates not the concentration at the time of such manufacture but the concentration at the time of an activity about the constituent for polish.

[0039] The following explains the constituent for polish of this invention concretely using an example.

[0040] In addition, this invention is not limited to the configuration of many examples explained below, unless the summary is exceeded.

[0041]

[Embodiment of the Invention]

<the content of the constituent for polish, and preparation> -- first, water was made to distribute fumed silica (50nm of diameters of a primary particle, 200nm of diameters of an aggregated particle), using an agitator as abrasives, and the slurry of 15 % of the weight of abrasives concentration was prepared. Subsequently, an acid compound and ammonia (basic compound) were added, and the sample of examples 1-8 and the examples 1-2 of a comparison was prepared so that it might become the concentration or the content indicated to this slurry at a table 1.

[0042] Here, acid concentration expresses with mol concentration the concentration of the acid compound dissolved in the constituent for polish, and an ammonia content expresses with mol concentration the total amount of the ammonia dissolved in the constituent for polish.

[0043] The polish trial by the sample of <a polish trial> next examples 1-8, and the examples 1-2 of a comparison was performed. As a workpiece, the base of the 6 inch silicon wafer (outer diameter of about 150mm) which formed the silicon-dioxide film with the CVD method was used, and the field with the film of the silicon-dioxide film was ground.

[0044] Polish was performed using the one side grinder (570mm of diameters of a surface plate). The scouring pad which stuck the urethane foam pad (ICmade from Rodel (U.S.)- 1000) on the nonwoven fabric pad (Suba400 made from Rodel (U.S.)) was stuck on the surface plate of a grinder, and it loaded with the wafer with the silicon-dioxide film, and ground for 3 minutes.

[0045] Polish conditions were set to a part for /, and processing pressure force 490 g/cm², rotating speed 35rpm, and constituent amount-of-supply wafer rotational frequency of 150 cc 70rpm for polish.

[0046] After polish, after sequential-washing the wafer and drying, the polish rate was found according to each trial by measuring 49 decreases of thickness of a wafer, i.e., the machining allowance by polish,

averaging it, and σ (ing) by polish time amount.

[0047] From the machining allowance of 49 points called for by the above, N-U which is the homogeneous valuation basis of a polished surface was calculated by the degree type.

$N-U(\%) = \frac{R. (max) - R. (min)}{R. (ave) - x2} \times 100$ -- in the maximum machining allowance and R. (min), in the x100 top type, the minimum machining allowance and R. (ave) express [R. (max)] the average machining allowance.

[0048] N-U is an index showing the irregularity on the front face of a wafer by dispersion in the decrease of thickness generated in polish, i.e., the heterogeneity of a machining allowance, so that clearly also from this formula. The polished surface where the value of this N-U is larger has larger dispersion in the machining allowance by polish, and the polished surface where the value of N-U is smaller has conversely smaller dispersion in the machining allowance by polish.

[0049]

table 1 Ammonia The class of acid Acid compound Polish rate N-U A content Concentration [mol/l] [mol/l] [A part for nm/] [%] Example 1 0.0347 A nitric acid 0.0086 147 5.8 examples 2 0.0347 A hydrochloric acid 0.0086 151 5.6 examples 3 0.0347 sulfuric acids 0.0086 156 5.2 examples 4 0.0347 A phosphoric acid 0.0086 155 5.3 examples 5 0.0347 Formic acid 0.0086 153 5.6 examples 6 0.0347 acetic acids 0.0086 151 5.8 examples 7 0.0347 Maleic acid 0.0086 157 5.1 example 8 0.0347 Glycolic acid 0.0086 154 The example 1 of 6.5 comparisons 0.3071 - -143 Example 2 of 14.7 comparisons 0.0347 - - 135 6.6 [0050] The conventional constituent for polish has a polish rate remarkably smaller than the result shown in a table 1 as compared with the constituent for polish of this invention, or N-U is remarkably inferior, and it turns out that the constituent for polish of this invention is compatible in the outstanding polish rate and the homogeneity of the outstanding polished surface.

[0051] In addition, although not carried in the above-mentioned table 1, when viewing estimated the ground processing side used by these trials, an example and the example of a comparison were not found out about the surface discontinuity of a scratch and others.

[0052]

[Effect of the Invention] The constituent for polish of this invention has a large polish rate, and it is as having described above in the term of [Summary of the Invention] that the polished surface excellent in homogeneity can be made to form.

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TECHNICAL FIELD

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[0002] In more detail, in polish of the silicon-dioxide film which is an insulator layer for the interlayer insulation film and isolation to which the CMP technique (detail postscript) is applied conventionally, this invention can make the polish front face excellent in the homogeneity in a wafer form, and relates to the constituent for polish applicable to an advanced device formation technique at the same time a big polish rate is obtained.

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PRIOR ART

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[0004] Moreover, although compaction of the wire length by multilayering of a device is performed in order to cope with buildup of the wiring resistance by detailed-izing of wiring, the level difference on the formed front face of a pattern has been becoming an issue as a failure of multilayering.

[0005] In performing such detailed-izing and multilayering, it is required in that process to perform flattening on the front face of a request for removing a level difference, and a spin-on glass, resist etchback, and other flattening methods were used as this technique until now.

[0006] However, by such technique, although partial flattening is possible, it is in a difficult situation to attain global pre nari ZESHON (perfect flattening) required of a next-generation device, and flattening (it is called "CMP" Chemical Mechanical Polishing and the following) by mechanical mechanochemical-polishing processing which was, carried out and combined physical polish and chemical polish is examined increasingly current.

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[0008] Conventionally, the constituent for polish containing the basic compound chosen from fumed silica, water and a potassium hydroxide, ammonia, and others has been used for polish of the silicon-dioxide film currently used for the insulator layer for an interlayer insulation film or isolation. When using such a constituent for polish, a polish rate can be enlarged if the quantity of the addition of a basic compound is increased.

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EFFECT OF THE INVENTION

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TECHNICAL PROBLEM

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MEANS

[Means for Solving the Problem]

[Summary of the Invention]

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[0013] [Concrete explanation of invention]

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[0015] There are alpha-alumina, delta alumina, theta alumina, kappa alumina, and a different thing like other gestalten also in an aluminum oxide. Moreover, there are some which are called a fumed alumina from a manufacturing method.

[0016] It sees in cerium oxide from a thing trivalent from the oxidation number, a tetravalent thing, and crystal system, and there is a thing of hexagonal system, a tesseral system, and a face-centered cubic system in it.

[0017] It sees in titanium oxide from crystal system, and there is a thing of titanium monoxide, 3 oxidization 2 titanium, a titanium dioxide, and others in it. Moreover, there are some which are called a fumed titania from a manufacturing method.

[0018] Silicon nitride has alpha-silicon nitride, beta-silicon nitride, amorphous silicon nitride, and a different thing like other gestalten.

[0019] A zirconium dioxide is seen from crystal system and has monoclinic system, tetragonal system, and an amorphous thing. Moreover, there are some which are called fumed zirconia from a manufacturing method.

[0020] A manganese dioxide is seen in gestalt and has alpha-manganese dioxide, beta-manganese dioxide, gamma-2 manganese oxide, delta-2 manganese oxide, epsilon-2 manganese oxide, eta-2 manganese oxide, and others.

[0021] These things can be combined and used for the constituent of this invention at arbitration if needed. When combining, especially the how to combine or rate to be used are not limited.

[0022] The above-mentioned abrasives grind a polished surface-ed according to an operation

[mechanical / as an abrasive grain]. among these, generally 5-500nm of 10-200nm of particle size of a silicon dioxide comes out preferably with the mean particle diameter called for from the specific surface area measured with the BET adsorption method. moreover, generally an aluminum oxide, a zirconium dioxide, titanium oxide, silicon nitride, and 10-5,000nm of 50-3,000nm of particle size of a manganese dioxide come out preferably with the mean particle diameter called for from the specific surface area measured with the BET adsorption method. furthermore, the particle size of cerium oxide is the mean particle diameter observed by the scanning electron microscope, and, generally comes out 50-3,000nm preferably 10-5,000nm.

[0023] A polish rate becomes extremely small and is not practical if smaller than the range which there is a between title of the surface roughness of the ground front face being large when the mean particle diameter of these abrasives is large across the range shown here, or a scratch occurring, and was shown in reverse here.

[0024] the content of the abrasives in the constituent for polish -- criteria [weight / of a constituent] -- carrying out -- less than 40 % of the weight -- it comes out one to 30% of the weight more preferably 0.1 to 40% of the weight. If remainder has few contents of abrasives, a polish rate will become small, when many [to remainder], it becomes impossible to maintain homogeneity distribution, constituent viscosity may become excessive, and handling may become difficult at reverse.

[0025] the constituent for polish of <anion> this invention -- the ion of a nitric acid, a nitrous acid, a hydrochloric acid, perchloric acid, a chloric acid, a chlorous acid, a hypochlorous acid, a boric acid, perboric acid, a sulfuric acid, a sulfurous acid, persulfuric acid, a phosphoric acid, phosphorous acid, hypophosphorous acid, a silicic acid, organic acids, and those hydro acid, or those mixture -- since -- it comes to contain at least one kind of anion chosen from the becoming group As for these anions, it is common to make it generate in the constituent for polish by dissolving the acid compound which dissolves in water and emits the aforementioned specific anion, i.e., an acid, and its salt. Moreover, since a main solvent is water, the above-mentioned ion may be made to generate in this invention by introducing into water directly the gas-like compound which dissolves in water and emits the aforementioned anion, for example, hydrochloric acid gas, a sulfur dioxide, and others.

[0026] The thing of arbitration can be used for the acid compound to be used if effectiveness of this invention is not spoiled. Specifically (1) nitric acid, a nitrous acid, a hydrochloric acid, perchloric acid, a chloric acid, a chlorous acid, A hypochlorous acid, a boric acid, perboric acid, a sulfuric acid, a sulfurous acid, persulfuric acid, a phosphoric acid, phosphorous acid, hypophosphorous acid, a silicic acid, or an organic acid (for example, a formic acid --), for example, a carboxylic acid An acetic acid, monochloroacetic acid, dichloroacetic acid, a trichloroacetic acid, a maleic acid, A fumaric acid, a glycolic acid, a citric acid, a malic acid, a lactic acid, a tartaric acid, a malonic acid, The ammonium salt of a succinic acid, a gluconic acid, a propionic acid, butanoic acid or a valeric acid, and the acid of (2) and (1), Hydrogen salt ** of two or more acids is mentioned for basicity among the acids of sodium salt, potassium salt, lithium salt, a beryllium salt, magnesium salt or a calcium salt (3), and (1). In these, especially hydro acid salt ** that consists of the ammonium salt of a nitric acid, a hydrochloric acid, a boric acid, a sulfuric acid, a phosphoric acid, a formic acid, an acetic acid, a trichloroacetic acid, a maleic acid, a fumaric acid, a glucol acid, a citric acid, a malic acid, a lactic acid, a tartaric acid, a malonic acid, a succinic acid, a gluconic acid, propionic acids, and these acids and potassium salt or a boric acid, a sulfuric acid, a phosphoric acid, a maleic acid, a fumaric acid, a glucol acid, a citric acid, a malic acid, a lactic acid, a tartaric acid, a malonic acid or a succinic acid, and ammonium ion or potassium ion is desirable. These acid compounds can also be used together at a rate of arbitration.

[0027] In the constituent for polish of this invention, although the concentration of the aforementioned specific anion is not limited unless the effectiveness of this invention is spoiled, it is desirable that the total amounts of the aforementioned specific anion are 1/2 in a mole ratio to the total amount of the below-mentioned cation as a relative amount with the cation mentioned later, and it is desirable that it is especially 1/1. [200-2] [100-1] Although it is in the inclination for a polish rate to become large by increasing the quantity of the content of a specific anion, since the dispersibility of abrasives may get worse when it increases too much, caution is required.

[0028] Although it is more desirable to the constituent for polish of this invention to introduce an anion into the constituent for polish by using a water-soluble (soluble) acid compound from points, such as handling nature, it is possible to use, if dissolving into the constituent for polish is possible even if it is a poorly soluble compound. In other words, it is not necessary to take into consideration the acid compound which the ratio of the total amount of the aforementioned specific anion and the total amount of a cation is an amount based on the anion which is dissolving, and is not dissolving.

[0029] The constituent for polish of <cation> this invention comes to contain a specific cation. In the constituent for polish of this invention, when used, these cations are the aforementioned specific anion or independent, and promote scouring according to an operation [KEMIKARU / as a polish accelerator].

[0030] The cation used in this invention is at least one kind of cation chosen from the group which consists of ammonium ion, alkali-metal ion, and alkaline-earth-metal ion. The ion (henceforth "inorganic alkali ion") chosen from the group which consists of NH_4^+ , Li^+ , Na^+ , K^+ , Be^{2+} , Mg^{2+} , and Ca^{2+} especially is desirable. Such ion is introduced into the constituent for polish by usually dissolving the basic compound which emits the aforementioned inorganic alkali ion into the constituent for polish. Although it will not be limited especially if the basic compound used here does not spoil the effectiveness of this invention, at least one kind of compound specifically chosen from the group which consists of a potassium hydroxide, ammonium hydroxide, a sodium hydroxide, a lithium hydroxide, hydroxylation beryllium, a magnesium hydroxide, and a calcium hydroxide is mentioned. These basic compounds can also be used together at a rate of arbitration. Moreover, about the above-mentioned basic compound, when metal ions other than the aforementioned inorganic alkali ion use the thing of very few high grades, since an impurity metal ion can be decreased in the constituent for polish, it is desirable.

[0031] the content of said cation of the constituent for polish of this invention -- the whole quantity of the constituent for polish -- receiving -- 0.001-0.15 mols/l. -- 0.01-0.075 mols [/] 0.005-0.1 mols /come out l. more preferably l. Although there is an inclination for a polish rate to become large by increasing the quantity of the content of said inorganic alkali ion, when many, it is in the inclination for the homogeneity of a polished surface to get worse. Furthermore, since the degree of amelioration to a polish rate etc. becomes small and may produce an economical demerit, caution is required.

[0032] The constituent for polish of <constituent for polish> this invention makes water mix and distribute the above-mentioned abrasives with desired content generally, and is prepared by carrying out the specified quantity dissolution of the compound which emits the aforementioned specific anion further, and the compound which emits the aforementioned inorganic alkali ion. The method of distributing or dissolving these components underwater is arbitrary, for example, it agitates with a wing formula agitator, or it is distributed by ultrasonic distribution. Moreover, the mixed sequence foreword of each of these components is arbitrary, and may perform first whichever of the dissolution of distribution of abrasives, and an acid compound or a basic compound, and may perform both simultaneously.

[0033] Moreover, on the occasion of preparation of the constituent for polish of this invention, various kinds of well-known additives may be added further the object which attains quality maintenance and stabilization of a product, the class of workpiece, processing conditions, and if needed on other polish processings.

[0034] That is, the following are mentioned as a suitable example of the additive added further.

(b) Celluloses, for example, a cellulose, a carboxymethyl cellulose, Hydroxyethyl cellulose and others,
 (b) water solubility alcohols, For example, ethanol, propanol, ethylene glycol, and others, A surface active agent, for example, alkylbenzene-sulfonic-acid soda, the formalin condensate of naphthalenesulfonic acid, (Ha) and -- in addition to this -- (**)-- the organic poly anion system matter, for example, a ligninsulfonic acid salt, and polyacrylate -- and -- in addition to this -- (**)-- water soluble polymers (emulsifier), for example, polyvinyl alcohol, -- and -- in addition to this -- a (**)-- germicide, for example, sodium alginate, -- and -- in addition to this .

[0035] Moreover, although a thing is included said bottom as abrasives, an acid compound, and a basic compound in addition to the abrasives contained to the constituent for polish of this invention there, an

acid compound, and a basic compound, it is also possible to be the objects other than the application of abrasives or a polish accelerator, for example, to use the thing of inside to others as further additive for sedimentation prevention of abrasives.

[0036] it usually comes out of the constituent for polish of this invention that pH is set to 4-10 by said addition of a principal component carried out. Although pH of the constituent for polish is changed by addition of various kinds of auxiliary additives, in order to make the effectiveness of this invention discover, it is desirable that pH is 4-10. Therefore, when pH of the constituent for polish shifts from the range of 4-10, it is desirable to add an acid or alkali and to adjust pH. Moreover, even if pH is within the limits of this, it is [other being reasons, for example, the preservation stability of the constituent for polish, being / of a polish object / the physical properties, and] sometimes desirable for it to be alike and to adjust pH more nearly further in addition to this.

[0037] In addition, although the constituent for polish of this invention can be applied to the base material of arbitration, such as various industrial products, such as a semi-conductor, a photo mask, various bases for memory hard disks, and synthetic resin, or a member of those, it is desirable to use for surface flattening processing of the device wafer especially in semiconductor industry etc.

[0038] Moreover, the constituent for polish of this invention can be prepared as a comparatively high-concentration undiluted solution, can carry out storage or transport, and it can also be diluted and used for it at the time of actual polish processing. When the above-mentioned desirable density range was indicated as a thing at the time of actual polish processing and it takes such operation, it cannot be overemphasized that it becomes a more high-concentration solution in the condition of carrying out storage or transport. Moreover, it is desirable to be manufactured with such a condensed gestalt from a viewpoint of handling nature. In addition, the concentration mentioned above indicates not the concentration at the time of such manufacture but the concentration at the time of an activity about the constituent for polish.

[0039] The following explains the constituent for polish of this invention concretely using an example.

[0040] In addition, this invention is not limited to the configuration of many examples explained below, unless the summary is exceeded.

[0041]

[Embodiment of the Invention]

<the content of the constituent for polish, and preparation> -- first, water was made to distribute fumed silica (50nm of diameters of a primary particle, 200nm of diameters of an aggregated particle), using an agitator as abrasives, and the slurry of 15 % of the weight of abrasives concentration was prepared. Subsequently, an acid compound and ammonia (basic compound) were added, and the sample of examples 1-8 and the examples 1-2 of a comparison was prepared so that it might become the concentration or the content indicated to this slurry at a table 1.

[0042] Here, acid concentration expresses with mol concentration the concentration of the acid compound dissolved in the constituent for polish, and an ammonia content expresses with mol concentration the total amount of the ammonia dissolved in the constituent for polish.

[0043] The polish trial by the sample of <a polish trial> next examples 1-8, and the examples 1-2 of a comparison was performed. As a workpiece, the base of the 6 inch silicon wafer (outer diameter of about 150mm) which formed the silicon-dioxide film with the CVD method was used, and the field with the film of the silicon-dioxide film was ground.

[0044] Polish was performed using the one side grinder (570mm of diameters of a surface plate). The scouring pad which stuck the urethane foam pad (ICmade from Rodel (U.S.)- 1000) on the nonwoven fabric pad (Suba400 made from Rodel (U.S.)) was stuck on the surface plate of a grinder, and it loaded with the wafer with the silicon-dioxide film, and ground for 3 minutes.

[0045] Polish conditions were set to a part for /, and processing pressure force 490 g/cm², rotating speed 35rpm, and constituent amount-of-supply wafer rotational frequency of 150 cc 70rpm for polish.

[0046] After polish, after sequential-washing the wafer and drying, the polish rate was found according to each trial by measuring 49 decreases of thickness of a wafer, i.e., the machining allowance by polish, averaging it, and *(ing) by polish time amount.

[0047] From the machining allowance of 49 points called for by the above, N-U which is the homogeneous valuation basis of a polished surface was calculated by the degree type.

$N-U(\%) = \frac{R(\max) - R(\min)}{R(\max) + R(\min)} \times 100$ -- in the maximum machining allowance and R. (min), in the x100 top type, the minimum machining allowance and R. (ave) express [R. (max)] the average machining allowance.

[0048] N-U is an index showing the irregularity on the front face of a wafer by dispersion in the decrease of thickness generated in polish, i.e., the heterogeneity of a machining allowance, so that clearly also from this formula. The polished surface where the value of this N-U is larger has larger dispersion in the machining allowance by polish, and the polished surface where the value of N-U is smaller has conversely smaller dispersion in the machining allowance by polish.

[0049]

table 1 Ammonia The class of acid Acid compound Polish rate N-U A content Concentration [mol/l] [mol/l] [A part for nm/] [%] Example 1 0.0347 A nitric acid 0.0086 147 5.8 examples 2 0.0347 A hydrochloric acid 0.0086 151 5.6 examples 3 0.0347 sulfuric acids 0.0086 156 5.2 examples 4 0.0347 A phosphoric acid 0.0086 155 5.3 examples 5 0.0347 Formic acid 0.0086 153 5.6 examples 6 0.0347 acetic acids 0.0086 151 5.8 examples 7 0.0347 Maleic acid 0.0086 157 5.1 example 8 0.0347 Glycolic acid 0.0086 154 The example 1 of 6.5 comparisons 0.3071 - -143 Example 2 of 14.7 comparisons 0.0347 - - 135 6.6 [0050] The conventional constituent for polish has a polish rate remarkably smaller than the result shown in a table 1 as compared with the constituent for polish of this invention, or N-U is remarkably inferior, and it turns out that the constituent for polish of this invention is compatible in the outstanding polish rate and the homogeneity of the outstanding polished surface.

[0051] In addition, although not carried in the above-mentioned table 1, when viewing estimated the ground processing side used by these trials, an example and the example of a comparison were not found out about the surface discontinuity of a scratch and others.

[Translation done.]

DERWENT-ACC-NO: 1999-267437
DERWENT-WEEK: 199923
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TITLE: Abrasive composition used for polishing industrial products e.g. semiconductors - contains water, abrasive material, anion(s) selected from anions of e.g. peroxoboric acid, hydrochloric acid, sulphuric acid, at least one kind of cation selected from ammonium ion, alkali(earth) metal ions

PRIORITY-DATA: 1997JP-0244333 (September 9, 1997)

Search Selected

Search All

Clear

PATENT-FAMILY:

PUB-NO

PUB-DATE

LANGUAGE

PAGES

MAIN-IPC

☐ JP 11080708 A

March 26, 1999

006

C09K003/14

INT-CL (IPC): B24 B 37/00; C09 K 3/14; C09 K 13/04; G11 B 5/84; H01 L 21/304

ABSTRACTED-PUB-NO: JP 11080708A
BASIC-ABSTRACT:

An abrasive composition (P) contains water (A), abrasive material (B), at least one kind of anion (C) selected from the anions of HNO₃, HNO₂, HCl, HClO₄, HClO₃, HClO₂, HPH₂O₂, H₄SiO₄, organic acids, and anions of hydroacids, and their mixtures, at least one kind of cation (D) selected from ammonium ion, alkali metal ions, alkaline earth metal ions and a content of (D) is 0.001-0.12 mol/litre.

USE - (P) is suitable for polishing various industrial products like semiconductors, photomasks, substrates for memory hard disks, their parts, synthetic resin products.

ADVANTAGE - (P) can provide high speed polishing and polished surfaces excellent in uniformity.

Supplemental

L1: Entry 1 of 4

File: JPAB

Mar 26, 1999

PUB-NO: JP411080708A

DOCUMENT-IDENTIFIER: JP 11080708 A

TITLE: COMPOSITION FOR POLISHING

PUBN-DATE: March 26, 1999

INVENTOR-INFORMATION:
NAME

SUZUMURA, SATOSHI
TAMAI, KAZUMASA

COUNTRY

INT-CL (IPC):

C09 K 3/14; B24 B 37/00; C09 K 13/04; C09 K 13/04; H01 L 21/304; G11 B 5/84

ABSTRACT:

PROBLEM TO BE SOLVED: To obtain a composition for polishing, having a high polishing rate and capable of forming a polished surface excellent in uniformity.

SOLUTION: This composition for polishing comprises (1) water, (2) a polishing material, (3) at least one anion selected from the group consisting of nitrate, nitrite, chloride, perchlorate, chlorate, chlorite, hypochlorite, borate, silicate, sulfate, sulfite, persulfate, phosphate, phosphite, hypophosphite, thereof and (4) at least one cation selected from the group consisting of ammonium ions, alkali metallic ions and alkaline earth metallic ions. In this case, the total amount of the cation (4) is 0.001-0.15 mol/L.

L13 ANSWER 39 OF 53 CAPLUS COPYRIGHT 2004 ACS on STN

Full Text

AN 1999:207223 CAPLUS

DN 130:256169

TI

Abrasive compositions for polishing semiconductor wafers

IN

Suzumura, Satoshi; Tamai, Kazushige

PA

Fujimi, Inc., Japan

SO

Jpn. Kokai Tokkyo Koho, 6 pp.

DT

CODEN: JKXXAF

LA

Patent

Japanese

FAN.CNT 1

PATENT NO.

PI JP 11080708
PRAI JP 1997-244333

AB

The title comps. comprise (1) water, (2) abrasives, (3) 21 of

KIND DATE
A2 19990326
19970909

APPLICATION NO.

JP 1997-244333

DATE

19970909

The title comps. comprise (1) water, (2) abrasives, (3) 21 of
anions of HNO₃, HNO₂, HCl, HClO₄, HClO₃, HClO₂, HClO, H₃BO₃, perboric
acid, H₂SO₄, H₂SO₃, persulfuric acid, H₃PO₄, phosphorus acid,
hypophosphorous acid, silicic acid, and org. acid or its hydroacid, and
(4) 21 of cations selected from NH₄⁺, alkali metal ions, and alk.
earth ions as total 0.001-0.15 mol/L. The comps. provide high-speed
grinding with good surface uniformity.

STN Columbus

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平11-80708

(43) 公開日 平成11年(1999) 3月26日

(51) Int.Cl. ⁶	識別記号	F I	
C 0 9 K 3/14	5 5 0	C 0 9 K 3/14	5 5 0 D
			5 5 0 Z
B 2 4 B 37/00		B 2 4 B 37/00	H
C 0 9 K 13/04	1 0 1	C 0 9 K 13/04	1 0 1
	1 0 2		1 0 2

審査請求 未請求 請求項の数 7 O L (全 6 頁) 最終頁に続く

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(54) 【発明の名称】 研磨用組成物

(57) 【要約】

【課題】 研磨速度が大きく、均一性が優れた研磨面を形成させることができる研磨用組成物の提供。

【解決手段】 (1) 水、(2) 研磨材、(3) 硝酸、亜硝酸、塩酸、過塩素酸、塩素酸、亜塩素酸、次亜塩素酸、ホウ酸、過ホウ酸、硫酸、亜硫酸、過硫酸、リン酸、亜リン酸、次亜リン酸、ケイ酸、有機酸、およびそれらの水素酸のイオン、またはそれらの混合物、からなる群から選ばれる、少なくとも1種類の陰イオン、(4) アンモニウムイオン、アルカリ金属イオン、およびアルカリ土類金属イオンからなる群から選ばれる、少なくとも1種類の陽イオン。を含んでなる研磨用組成物であって、(4) の陽イオンの総量が0.001~0.15モル/リットルであることを特徴とする研磨用組成物。

【特許請求の範囲】

【請求項1】(1)水、(2)研磨材、(3)硝酸、亜硝酸、塩酸、過塩素酸、塩素酸、亜塩素酸、次亜塩素酸、ホウ酸、過ホウ酸、硫酸、亜硫酸、過硫酸、リン酸、亜リン酸、次亜リン酸、ケイ酸、有機酸、およびそれらの水素酸のイオン、またはそれらの混合物、からなる群から選ばれる、少なくとも1種類の陰イオン、

(4)アンモニウムイオン、アルカリ金属イオン、およびアルカリ土類金属イオンからなる群から選ばれる、少なくとも1種類の陽イオン。を含んでなる研磨用組成物であって、(4)の陽イオンの総量が0.001~0.15モル/リットルであることを特徴とする研磨用組成物。

【請求項2】研磨材の含有量が、研磨用組成物の重量を基準にして、40重量%未満である請求項1に記載の研磨用組成物。

【請求項3】研磨材が、二酸化ケイ素、酸化アルミニウム、酸化セリウム、酸化チタン、窒化ケイ素、酸化ジルコニウム、および二酸化マンガンからなる群より選ばれる少なくとも1種類の研磨材である、請求項1または2のいずれかに記載の研磨用組成物。

【請求項4】陽イオンが、 NH_4^+ 、 Li^+ 、 Na^+ 、 K^+ 、 Be^{2+} 、 Mg^{2+} 、および Ca^{2+} からなる群より選ばれる少なくとも1種類の陽イオンである、請求項1~3のいずれか1項に記載の研磨用組成物。

【請求項5】陽イオンの総量が、0.005~0.1モル/リットルである、請求項1~4のいずれか1項に記載の研磨用組成物。

【請求項6】陽イオンの総量が、0.01~0.075モル/リットルである、請求項1~4のいずれか1項に記載の研磨用組成物。

【請求項7】前記陰イオンの総量が、前記陽イオンに対して、モル比で1/200~2である、請求項1~6のいずれか1項に記載の研磨用組成物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、半導体、フォトリソマスク、各種メモリーハードディスク用基盤および合成樹脂等各種工業製品またはその部材の研磨に使用される研磨用組成物に関し、特に半導体産業等におけるデバイスウェーハの表面平坦化加工に好適な研磨用組成物に関するものである。

【0002】さらに詳しくは、本発明は、従来よりCMP技術(詳細後記)が適用されている、層間絶縁膜および素子分離のための絶縁膜である二酸化ケイ素膜の研磨において、大きな研磨速度が得られると同時に、ウェーハ内の均一性が優れた研磨表面を形成させることができ、高度なデバイス形成技術に適用可能な研磨用組成物に関するものである。

【0003】

【従来の技術】近年のコンピューターを始めとする所謂ハイテク製品の進歩は目覚ましく、これに使用される部品、例えばULSI、は年々高集積化・高速化の一途をたどっている。これに伴い、半導体装置のデザインルールは年々微細化が進み、デバイス製造プロセスでの焦点深度は浅くなり、パターン形成面に要求される平坦性は厳しくなっている。

【0004】また、配線の微細化による配線抵抗の増大に対処するため、デバイスの多層化による配線長の短縮が行われているが、形成されたパターン表面の段差が多層化の障害として問題化してきている。

【0005】このような微細化および多層化を行うに当たっては、そのプロセス中で段差を取り除くための所望表面の平坦化を行うことが必要であり、この手法として、これまではスピンドングラス、レジストエッチバックおよびその他の平坦化法が用いられていた。

【0006】しかし、これらの手法では、部分的な平坦化は可能であるが、次世代のデバイスに要求されるグローバルレナリゼーション(完全平坦化)を達成することは困難な状況であり、現在では機械的ないし物理的研磨と化学的研磨とを組み合わせたメカノケミカル研磨加工による平坦化(Cheical Mechanical Polishing、以下「CMP」という)が検討されるようになってきている。

【0007】このような研磨技術を用いて、層間絶縁膜または素子分離のための絶縁膜である二酸化ケイ素膜の平坦化を実施するに当たっての技術課題は、平坦化加工する面を研磨による取代の過不足なく均一に仕上げること、および大きな研磨速度で研磨することにより生産性を向上させることである。

【0008】従来、層間絶縁膜または素子分離のための絶縁膜に使用されている二酸化ケイ素膜の研磨には、フェムドシリカ、水、および水酸化カリウム、アンモニアおよびその他から選ばれた塩基性化合物を含む研磨用組成物が用いられてきた。このような研磨用組成物を用いる場合、塩基性化合物の添加量を増量すると研磨速度を大きくすることができる。

【0009】これは、このような研磨加工において、化学的な研磨作用が利用されているためである。化学的な研磨作用とは、上記の研磨加工を例にとれば、二酸化ケイ素膜が、化学的研磨促進剤である塩基性化合物の効果により化学的な侵食を受けて、研磨による除去を受けやすくなることをいう。すなわち、上記の研磨加工において、塩基性化合物の添加量を増量することにより化学的な作用が増大して、全体の研磨速度が大きくなるのである。

【0010】

【発明が解決しようとする課題】しかしながら、本発明者らの知る限り、上記したような従来の研磨用組成物においては、通常、比較的多量の塩基性化合物を含んでお

り、必要レベルの研磨速度は維持されているものの、研磨面の均一性においては十分満足なレベルにすることができず、まだ改良の余地があった。従って、十分な研磨速度と、研磨面の均一性とを両立できる研磨用組成物が望まれていた。

【0011】

【課題を解決するための手段】

【発明の概要】

＜要旨＞本発明の研磨用組成物は、(1)水、(2)研磨材、(3)硝酸、亜硝酸、塩酸、過塩素酸、塩素酸、亜塩素酸、次亜塩素酸、ホウ酸、過ホウ酸、硫酸、亜硫酸、過硫酸、リン酸、亜リン酸、次亜リン酸、ケイ酸、有機酸、およびそれらの水素酸のイオン、またはそれらの混合物、からなる群から選ばれる、少なくとも1種類の陰イオン、(4)アンモニウムイオン、アルカリ金属イオン、およびアルカリ土類金属イオンからなる群から選ばれる、少なくとも1種類の陽イオン、を含んでなる研磨用組成物であって、(4)の陽イオンの総量が0.001～0.15モル/リットルであること、を特徴とするものである。

【0012】＜効果＞本発明の研磨用組成物は、研磨速度が大きく、同時に均一性が優れた研磨面を形成させることができる。

【0013】【発明の具体的説明】

＜研磨材＞本発明の研磨用組成物において研磨材として用いるのに適当な研磨材は、二酸化ケイ素、酸化アルミニウム、酸化セリウム、酸化チタン、窒化ケイ素、酸化ジルコニウム、および二酸化マンガンの群から選ばれるものである。

【0014】本発明において、もちいることのできる二酸化ケイ素には、コロイダルシリカ、フェームドシリカ、およびその他の、製造法や性状の異なるものが多種存在する。

【0015】酸化アルミニウムにも、 α -アルミナ、 δ -アルミナ、 θ -アルミナ、 κ -アルミナ、およびその他の形態的に異なるものがある。また製造法からフェームドアルミナと呼ばれるものもある。

【0016】酸化セリウムには、酸化数から3価のものと4価のもの、また結晶系から見て、六方晶系、等軸晶系、および面心立方晶系のものがある。

【0017】酸化チタンには、結晶系から見て、一酸化チタン、三酸化二チタン、二酸化チタンおよびその他のものがある。また製造法からフェームドチタニアと呼ばれるものもある。

【0018】窒化ケイ素は、 α -窒化ケイ素、 β -窒化ケイ素、アモルファス窒化ケイ素、およびその他の形態的に異なるものがある。

【0019】酸化ジルコニウムは、結晶系から見て、単斜晶系、正方晶系、および非晶質のものがある。また、製造法からフェームドジルコニアと呼ばれるものもある。

る。

【0020】二酸化マンガンは、形態的に見て α -二酸化マンガ、 β -二酸化マンガ、 γ -二酸化マンガ、 δ -二酸化マンガ、 ϵ -二酸化マンガ、 η -二酸化マンガ、および他がある。

【0021】本発明の組成物には、これらのものを任意に、必要に応じて組み合わせ、用いることができる。組み合わせる場合には、その組み合わせ方や使用する割合は特に限定されない。

【0022】上記の研磨材は、砥粒としてメカニカルな作用により被研磨面を研磨するものである。このうち二酸化ケイ素の粒径は、BET法により測定した比表面積から求められる平均粒子径で一般に5～500nm、好ましくは10～200nm、である。また、酸化アルミニウム、酸化ジルコニウム、酸化チタン、窒化ケイ素、および二酸化マンガンの粒径は、BET法により測定した比表面積から求められる平均粒子径で一般に10～5,000nm、好ましくは50～3,000nm、である。さらに、酸化セリウムの粒径は、走査型電子顕微鏡により観察される平均粒子径で、一般に10～5,000nm、好ましくは50～3,000nm、である。

【0023】これらの研磨材の平均粒子径がここに示した範囲を超えて大きいと、研磨された表面の表面粗さが大きかったり、スクラッチが発生したりするなどの問題があり、逆に、ここに示した範囲よりも小さいと研磨速度が極端に小さくなってしまい実用的でない。

【0024】研磨用組成物中の研磨材の含有量は、組成物の重量を基準にして、40重量%未満、好ましくは0.1～40重量%、より好ましくは1～30重量%、である。研磨材の含有量が余りに少ないと研磨速度が小さくなり、逆に余りに多いと均一分散が保てなくなり、かつ組成物粘度が過大となって取扱いが困難となることがある。

【0025】＜陰イオン＞本発明の研磨用組成物は、硝酸、亜硝酸、塩酸、過塩素酸、塩素酸、亜塩素酸、次亜塩素酸、ホウ酸、過ホウ酸、硫酸、亜硫酸、過硫酸、リン酸、亜リン酸、次亜リン酸、ケイ酸、有機酸、およびそれらの水素酸のイオン、またはそれらの混合物、からなる群より選ばれる少なくとも1種類の陰イオンを含んでなる。これらの陰イオンは、水に溶解して前記の特定の陰イオンを放出する酸化合物、すなわち、酸、またはその塩、を溶解することにより研磨用組成物中に生成させるのが普通である。また、本発明において、主たる溶媒は水であるので、水に溶解して前記の陰イオンを放出する、気体状化合物、例えば塩酸ガス、亜硫酸ガス、およびその他、を水に直接導入することで上記のイオンを生成させてもよい。

【0026】用いる酸化合物は、本発明の効果を損なわないのであれば任意のものをを用いることができる。具体的には、(1)硝酸、亜硝酸、塩酸、過塩素酸、塩素

酸、亜塩素酸、次亜塩素酸、ホウ酸、過ホウ酸、硫酸、亜硫酸、過硫酸、リン酸、亜リン酸、次亜リン酸、ケイ酸、または有機酸、例えばカルボン酸（例えば、ギ酸、酢酸、モノクロロ酢酸、ジクロロ酢酸、トリクロロ酢酸、マレイン酸、フマル酸、グリコール酸、クエン酸、リンゴ酸、乳酸、酒石酸、マロン酸、コハク酸、グルコン酸、アロピオン酸、酪酸、または吉草酸）、(2)

(1)の酸のアンモニウム塩、ナトリウム塩、カリウム塩、リチウム塩、ベリリウム塩、マグネシウム塩、またはカルシウム塩(3)(1)の酸の内、塩基度が2以上の酸の水素塩、が挙げられる。これらの中で、硝酸、塩酸、ホウ酸、硫酸、リン酸、ギ酸、酢酸、トリクロロ酢酸、マレイン酸、フマル酸、グリコール酸、クエン酸、リンゴ酸、乳酸、酒石酸、マロン酸、コハク酸、グルコン酸、アロピオン酸、およびこれらの酸のアンモニウム塩ならびにカリウム塩、あるいはホウ酸、硫酸、リン酸、マレイン酸、フマル酸、グリコール酸、クエン酸、リンゴ酸、乳酸、酒石酸、マロン酸、またはコハク酸と、アンモニウムイオンまたはカリウムイオンとからなる水素酸塩、が特に好ましい。これらの酸化合物は任意の割合で併用することもできる。

【0027】本発明の研磨用組成物において、前記の特定の陰イオンの濃度は、本発明の効果を損なわない限り限定されないが、後述する陽イオンとの相対量として、前記の特定の陰イオンの総量が、後述の陽イオンの総量に対して、モル比で1/200~2であることが好ましく、1/100~1であることが特に好ましい。特定の陰イオンの含有量を増量することで研磨速度が大きくなる傾向にあるが、過度に増量すると研磨材の分散性が悪化することもあるので注意が必要である。

【0028】本発明の研磨用組成物には、取り扱い性などの点から、水溶性（易溶性）の酸化合物を用いることにより、研磨用組成物に陰イオンを導入することがより好ましいが、難溶性の化合物であっても研磨用組成物中に溶解することが可能なものであれば用いることが可能である。言い換えれば、前記の特定の陰イオンの総量と陽イオンの総量の比率は、溶解している陰イオンをもとにした量であり、溶解していない酸化合物は考慮する必要がない。

【0029】＜陽イオン＞本発明の研磨用組成物は、特定の陽イオンを含んでなる。本発明の研磨用組成物において、これらの陽イオンは、用いられる場合には、前記の特定の陰イオンとともに、または単独で、研磨促進剤としてケミカルな作用により研磨作用を促進するものである。

【0030】本発明において用いられる陽イオンは、アンモニウムイオン、アルカリ金属イオン、およびアルカリ土類金属イオンからなる群から選ばれる、少なくとも1種類の陽イオンである。特に、 NH_4^+ 、 Li^+ 、 Na^+ 、 K^+ 、 Be^{2+} 、 Mg^{2+} 、および Ca^{2+} からなる群か

ら選ばれるイオン（以下、「無機アルカリイオン」という）が好ましい。このようなイオンは、通常、前記の無機アルカリイオンを放出する塩基性化合物を研磨用組成物中に溶解させることにより、研磨用組成物中に導入される。ここで用いられる塩基性化合物は、本発明の効果を損なわないものであれば特に限定されないが、具体的には、水酸化カリウム、水酸化アンモニウム、水酸化ナトリウム、水酸化リチウム、水酸化ベリリウム、水酸化マグネシウム、および水酸化カルシウムからなる群から選ばれる少なくとも1種類の化合物が挙げられる。これらの塩基性化合物は任意の割合で併用することもできる。また、上記の塩基性化合物については、前記の無機アルカリイオン以外の金属イオンが極めて少ない高純度のものを使用することにより、研磨用組成物中に不純物金属イオンを減少させることができるので好ましい。

【0031】本発明の研磨用組成物の前記陽イオンの含有量は、研磨用組成物の全量に対して、0.001~0.15モル/リットル、好ましくは0.005~0.1モル/リットル、より好ましくは、0.01~0.075モル/リットル、である。前記無機アルカリイオンの含有量を増量することで研磨速度が大きくなる傾向があるが、多いと研磨面の均一性が悪化する傾向にある。さらには、研磨速度などに対する改良の度合いが小さくなり、経済的なデメリットを生じることもあり得るので注意が必要である。

【0032】＜研磨用組成物＞本発明の研磨用組成物は、一般に上記の研磨材を所望の含有率で水に混合し、分散させ、さらに前記の特定の陰イオンを放出する化合物、および前記の無機アルカリイオンを放出する化合物を所定量溶解させることにより調製する。これらの成分を水中に分散または溶解させる方法は任意であり、例えば、翼式攪拌機で攪拌したり、超音波分散により分散させる。また、これらの各成分の混合順序は任意であり、研磨材の分散と、酸化合物または塩基性化合物の溶解のどちらを先に行ってもよく、また両者を同時に行ってもよい。

【0033】また、本発明の研磨用組成物の調製に際しては、製品の品質保持や安定化を図る目的や、被加工物の種類、加工条件およびその他の研磨加工上の必要に応じて、各種の公知の添加剤をさらに加えてもよい。

【0034】すなわち、さらに加える添加剤の好適な例としては、下記のものが挙げられる。

(イ) セルロース類、例えばセルロース、カルボキシメチルセルロース、ヒドロキシエチルセルロース、およびその他、(ロ) 水溶性アルコール類、例えばエタノール、プロパノール、エチレングリコール、およびその他、(ハ) 界面活性剤、例えばアルキルベンゼンスルホン酸ソーダ、ナフタリンスルホン酸のホルマリン縮合物、およびその他、(ニ) 有機ポリアニオン系物質、例えばリグニンスルホン酸塩、ポリアクリル酸塩、および

その他、(ホ)水溶性高分子(乳化剤)類、例えばポリビニルアルコール、およびその他、(ヘ)殺菌剤、例えばアルギン酸ナトリウム、およびその他。

【0035】また、本発明の研磨用組成物に対して、そこに含まれる研磨材、酸化合物、および塩基性化合物に加えて、研磨材、酸化合物、および塩基性化合物として前記したものを包含するものの中からその他のものを、研磨材または研磨促進剤の用途以外の目的で、例えば研磨材の沈降防止のために、さらなる添加剤として用いることも可能である。

【0036】本発明の研磨用組成物は、前記した主成分の添加により、pHが4~10となるのが普通である。各種の補助添加剤の添加により研磨用組成物のpHは変動するが、本発明の効果を発現させるためにはpHが4~10であることが好ましい。従って、研磨用組成物のpHが4~10の範囲からはずれてしまう場合、酸またはアルカリを添加してpHを調整することが好ましい。また、pHがこの範囲内にあっても、その他の理由、例えば研磨用組成物の保存安定性、研磨対象物の物性、およびその他、によりさらにpHを調整することが好ましいこともある。

【0037】なお、本発明の研磨用組成物は、半導体、フォトマスク、各種メモリーハードディスク用基盤および合成樹脂等各種工業製品またはその部材などの任意の基材に対して適用することが可能であるが、特に半導体産業等におけるデバイスウェーハの表面平坦化加工に用いることが好ましい。

【0038】また、本発明の研磨用組成物は、比較的高濃度の原液として調製して貯蔵または輸送などをし、実際の研磨加工時に希釈して使用することもできる。前述の好ましい濃度範囲は、実際の研磨加工時のものとして記載したのであり、このような使用方法をとる場合、貯蔵または輸送などをされる状態においてはより高濃度の溶液となることは言うまでもない。また、取り扱い性の観点から、そのような濃縮された形態で製造されることが好ましい。なお、研磨用組成物について前述した濃度などは、このような製造時の濃度ではなく、使用時の濃度を記載したものである。

【0039】以下は、本発明の研磨用組成物を例を用いて具体的に説明するものである。

【0040】なお、本発明は、その要旨を超えない限り、以下に説明する諸例の構成に限定されない。

【0041】

【発明の実施の形態】

表1

	アンモニア 含有量 [mol/l]	酸の種類	酸化合物 濃度 [mol/l]	研磨速度 [nm/分]	N-U [%]
実施例1	0.0347	硝酸	0.0086	147	5.8
実施例2	0.0347	塩酸	0.0086	151	5.6

*＜研磨用組成物の内容および調製＞まず、研磨材としてフュームドシリカ(一次粒子径50nm、二次粒子径200nm)を攪拌機を用いて水に分散させて、研磨材濃度15重量%のスラリーを調製した。次いでこのスラリーに表1に記載した濃度または含有量となるように酸化合物およびアンモニア(塩基性化合物)を添加して実施例1~8および比較例1~2の試料を調製した。

【0042】ここで、酸濃度とは、研磨用組成物中に溶存している酸化合物の濃度をモル濃度で表したものであり、アンモニア含有量とは研磨用組成物中に溶存しているアンモニアの総量をモル濃度で表したものである。

【0043】＜研磨試験＞次に、実施例1~8および比較例1~2の試料による研磨試験を行った。被加工物としては、CVD法により二酸化ケイ素膜を成膜した6インチ・シリコンウェーハ(外径約150mm)の基盤を使用し、二酸化ケイ素膜の膜付き面を研磨した。

【0044】研磨は片面研磨機(定盤径570mm)を使用して行った。研磨機の定盤には不織布パッド(Rodel社(米国)製Suba400)上に発泡ウレタンパッド(Rodel社(米国)製IC-1000)を貼り合わせた研磨パッドを貼り付け、二酸化ケイ素膜付ウェーハを装填して3分間研磨した。

【0045】研磨条件は、加工圧力490g/cm²、定盤回転数35rpm、研磨用組成物供給量150cc/分、ウェーハ回転数70rpmとした。

【0046】研磨後、ウェーハを順次洗浄、乾燥した後、ウェーハの膜厚減、すなわち研磨による取代を49点測定し、それを平均して研磨時間で除することにより、各試験別に研磨速度を求めた。

【0047】上記により求められた49点の取代から、次式により研磨面の均一性の評価基準であるN-Uを求めた。

$$N-U(\%) = \{R.(\max) - R.(\min)\} / \{R.(\text{ave}) \times 2\} \times 100$$

上式において、R.(max)は最大取代、R.(min)は最小取代、またR.(ave)は平均取代を表している。

【0048】この式からも明らかなように、N-Uとは研磨において発生する膜厚減のばらつきによるウェーハ表面の凹凸、すなわち取代の不均一性を表す指標である。このN-Uの値が大きい研磨面ほど研磨による取代のばらつきが大きく、逆にN-Uの値が小さい研磨面ほど研磨による取代のばらつきが小さい。

【0049】

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実施例3	0.0347	硫酸	0.0086	156	5.2
実施例4	0.0347	リン酸	0.0086	155	5.3
実施例5	0.0347	ギ酸	0.0086	153	5.6
実施例6	0.0347	酢酸	0.0086	151	5.8
実施例7	0.0347	マレイン酸	0.0086	157	5.1
実施例8	0.0347	グリコール酸	0.0086	154	6.5
比較例1	0.3071	—	—	143	14.7
比較例2	0.0347	—	—	135	6.6

【0050】表1に示した結果より、従来の研磨用組成物は、本発明の研磨用組成物に比較して、研磨速度が著しく小さいか、N-Uが著しく劣っており、本発明の研磨用組成物は優れた研磨速度と優れた研磨面の均一性とを両立していることがわかる。

【0051】なお、上記の表1において掲載しなかったが、これらの試験で用いた研磨済加工面を目視にて評価*

10*したところ、実施例、比較例ともに、スクラッチおよびその他の表面欠陥については見出されなかった。

【0052】

【発明の効果】本発明の研磨用組成物は、研磨速度が大きく、均一性が優れた研磨面を形成させることができることは、[発明の概要]の項に前記したとおりである。

フロントページの続き

(51)Int. Cl.⁶

H01L 21/304

// G11B 5/84

識別記号

321

F1

H01L 21/304

G11B 5/84

321P

A